

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: MICHEL, et al.

Docket: 2002DE142

Serial No. 10/533,999

Group Art Unit: 1796

Filed: 05/04/2005

Examiner: Khan, Amina S

For: Blue Dye With Particularly High Purity And Positive  
Triboelectric Control Effect

DECLARATION UNDER 37 CFR § 1.132

I, Dr. Hans-Tobias Macholdt, state that I am a resident of D-64297 Darmstadt-Eberstadt, Federal Republic of Germany; that I am a citizen of the Federal Republic of Germany; that I am a chemist having graduated at the University of Darmstadt, Federal Republic of Germany; that I am one of the inventors of U.S. Patent Application Serial No. 10/533,999; for "Blue dye with particularly high purity and positive triboelectric control effect"; that I am one of the inventors of US 5,061,585 and of US 6,168,895 cited as prior art against the beforementioned US Patent Application; that I consider myself qualified, by my knowledge of chemistry, and especially of triphenylmethane dyes, electrophotographic toners and developers and by my 20 years' experience in this field; that I can make the following observations and statements to wit:

This Declaration is to support by factual evidence the statements and observations of my June 26, 2008 declaration:

**(A) Aniline level according to US 3,671,553 (equivalent to German Patent 1,919,724; Papenfuss et al.)**

A solution of 100 g of a color base of the formula as shown in Example 9 in 38 g of aniline was diluted with 450 g of chlorobenzene (solution 1). As a precipitating solution (II) 104 g of 35% sulfuric acid were used. The two solutions were fed at a ratio of 5.65 : 1 by means of dosing pumps to a stirrer mixture regulated by thermostat to 60-70°C. The overflow vessel of the mixture was connected to a cascade formed by 3 vessels provided with stirrers. This cascade was also heated to 60-70°C. Its reaction volume was such that the product flowing over from the mixer resided therein for 50-60 min. The formation of the dyestuff suspension which had

begun in the mixer was complete after the passage through the cascade. This was continuously checked by taking a sample from the suspension which left the last cascade vessel. The freely overflowing sulfate suspension was conducted to a trough from which a rotary piston pump conveyed the same amount to a continuously operating drum rotary pressure filter as it received from the cascade. On the rotary filter the residue was also continuously washed with chlorobenzene of room temperature until the filtrate was colorless, then blown dry by means of nitrogen, and the press cake dropping off the filter was pasted up into a pumpable suspension in a continuously operating mashing device with 4 times the amount of water of 90°C calculated on the color base used. This suspension was conducted to another pump trough from which another rotary piston pump conveyed the dyestuff suspension to a connected distilling cascade at such a rate that the liquid level in the pump trough remained constant. The reaction volume of the cascade had to assure a residence time of the suspension of from 4-6 h. During this time chlorobenzene adhering to the presscake was distilled off azeotropically by blowing in steam. The suspension leaving the cascade after this time was free from chlorobenzene. It was conducted to the trough of a third rotary piston pump which conveyed it, while checking its level, to another continuously operating drum rotary pressure filter where the solid material was separated from the filtrate, washed with water of 90°C and blown dry by means of low-pressure steam. After homogenization in a paste mixer the continuous product stream leaving the filter was conducted to a continuously operating disk drier in which it was dried at 100-110°C to a residual moisture of 0.2 percent. About 80 g of a purified dyestuff sulfate were obtained.

Analytical HPLC method for determining aniline level:

Column: RP-select B;

Eluent: methanol/water, beginning with 30% methanol and 70% water, then graduating over the course of 20 min to 50% methanol; then to 100% methanol over the course of 10 min, then remaining constant at 100% methanol for 10 min;

Temperature: 40°C;

Flow rate: 0.2 ml/min.

Result:

9,000 ppm of aniline.

**(B) Aniline level according to US 5,061,585 (Macholdt et al.)**

This reference employs the same coloring agent as in US 3,671,553 (Papenfuss et al.); see Col. 4, line 11-12: "The preparation of the coloring agent according to the invention is described in German Patent 1,919,724" (which is equivalent to US 3,671,553).

Therefore, US 5,061,585 (Macholdt et al.) uses triphenylmethane dyes having the same aniline content as found above.

**(C) Aniline level according to US 6,168,895 (Metz et al.)**

This reference employs the same coloring agent as in US 5,061,585 (Macholdt et al.); see Col. 8, line 39-40: "Other suitable triphenylmethanes are those described in US Pat. No. 5,061,585, especially those of the formula (2)".

Therefore, US 6,168,895 (Metz et al.) uses triphenylmethane dyes having the same aniline content as found in US 5,061,585 (Macholdt et al.) which uses triphenylmethanes as prepared in US 3,671,553 (Papenfuss et al.) which have an aniline level of 9,000 ppm.

**(D) Aniline level according to US 3,652,602 (Schafer et al.)**

This reference discloses in Example 5 an early preparation method of a triphenylmethane dye which is the same dye as described in above mentioned US 3,671,553 (Papenfuss) and corresponding to the blue dye of formula (1) in instant U.S. Patent Application Serial No. 10/533,999.

Into a suspension of 49 g of anhydrous  $\text{FeCl}_3$  in 200 g of chlorobenzene 62.5 g of p-chlorobenzotrichloride were added dropwise within 3 h at 20°C to 25°C followed by stirring for 1 h and heating up to 55-60°C at which temperature the mixture was maintained for 5 h. After 1.5 h the complex iron compound crystallized out from the solution. After cooling to -5 to 10°C the excess of chlorobenzene was removed by filtration and the press cake washed with chlorobenzene.

Thereafter, 27.5 g of m-toluidine were added stirring the mixture for 2 h at 130°C. Then, 127 g of aniline were poured in and the mixture was stirred for 4 to 5 h at 150-155°C. Then, the melt was diluted with 100 ml of aniline, run into 1.5 l of sulfuric acid of 40% strength and the whole was stirred for 2-3 h at 90°C until the precipitated dyestuff had become finely grained. After filtering off with suction, washing to neutral and drying in vacuo, a dark violet powder was obtained. Yield about 145 g.

Analytical HPLC method for determining aniline level:

Column: RP-select B;

Eluent: methanol/water, beginning with 30% methanol and 70% water, then graduating over the course of 20 min to 50% methanol; then to 100% methanol over the course of 10 min, then remaining constant at 100% methanol for 10 min;

Temperature: 40°C;

Flow rate: 0.2 ml/min.

Result:

10,000 ppm of aniline.

**(D) Evaluation of the results:**

The most pertinent prior art references use triphenylmethane dyes which have been prepared according to Papenfuss et al. Although this reference discloses a sophisticated method of producing highly pure triphenylmethane dyes, the aniline content is still far above nowadays acceptable levels.

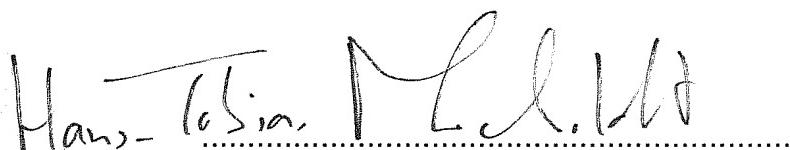
US 3,652,602 (Schafer et al.) was cited as prior art reference against U.S. Patent Application Serial No. 10/533,999. This document discloses a method for manufacturing triphenylrosaniline dyes which was 2 years prior to the method of Papenfuss. As could be expected, a significantly higher amount of aniline was detected in this product.

These experiments clearly demonstrate that not before the invention of U.S. Patent Application Serial No. 10/533,999 existed triphenylmethane colorants having aniline levels below 2,000 ppm.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Frankfurt on the Main

January 14, 2009



(Hans-Tobias Macholdt)